

Preparation and Spectroscopic Studies of Some Copper and Nickel Schiff Base Complexes and their Applications as Colouring Pigments in Protective Paints Industry

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NEW copper (II), nickel (II) Schiff base complexes derived from 3,3-dimethoxybenzidine and selected aldehydes, namely 2,4-dihydroxybenzaldehyde with the metal salts have been synthesized using a simple technique of microwave method (Green chemistry). The physical properties of prepared ligand and its metal complexes were recorded. The ligand and complexes were characterized using elemental analysis, NMR, infrared and also their geometrical structure were investigated using spectral UV-Vis reflectance, magnetic susceptibility, electron spin resonance (ESR), thermal gravimetric analysis (TGA) and scan electron microscope (SEM). The performance tests (oil absorption, fineness of grind, moisture content, and pH and bleeding test in different solvents) of the solid metal complexes were explored to ensure that the complexes can be used as a pigments in the field of anticorrosive paints without any compatibility problems in the paint's vehicle. The anticorrosive paints were formulated based on the prepared metal complexes as a pigments and the Physical, mechanical, colour properties and corrosion resistance of dry paint films were also examined. The obtained results revealed that the prepared metal complex pigments showed excellent mechanical, corrosion resistance with colour stability and did not effect or react with the other components in the anticorrosive paint formula.

Keywords: Transition metal complexes, Schiff bases, Pigments, paints, Corrosion resistance.

Coordination compounds of azomethine ligands are important objects of the modern chemistry of metal complexes and are considered in a series of monographs and reviews. An increased attention to complexes of azomethine compounds is due to the possibility of a wide variation of their ligand environment presented by aldehyde and amine moieties and the production of multifunctional materials from these compounds. Among such materials are magneto-active and luminescent complexes [1-3]. The most widespread

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protection of metal materials is the application of organic coatings created from anticorrosion paints. This method secures the chemical or electrochemical reaction of an anticorrosion pigment with a metal alone or with a corrosive agent penetrating through the protective organic coating [4]. Metal complex pigments are mainly used in paints, and the products are fast enough to be applied especially in industrial finishes. In view of this, we described the synthesis and characterization of Schiff base and its copper (II) and nickel (II) complexes. Also, the applications of the prepared complexes as colouring pigments and their corrosion behavior were studied.

Experimental

Materials and instruments

All chemicals and solvents used were of BDH and sigma-Aldrich and used without further purification. ¹HNMR spectra in D6-DMSO with TMS as internal standard were obtained from a Jeol- FX-90Q Fourier NMR spectrometer and the Fourier transform infrared (FT-IR) spectra were recorded on a single-beam spectrometer (Bruker, Vector 22, Germany) with a resolution of 4 cm⁻¹ at the central laboratories of the Egyptian Armed Forces, Egypt. Elemental analysis for carbon, hydrogen and nitrogen were determined by Perkin-Elmer 2400 at the central laboratories of the Egyptian Armed Forces. An Ultra violet spectra (Shimadzu UV-2600/2700), Electron Spin Resonance (ESR, EMX 1444 EPR), Thermal Gravimetric Analysis (TGA, Shimadzu's TGA-50/51) measurements were carried out at Egyptian Atomic Energy Authority. Finally, Scan Electron Microscope (SEM, Quanta 250 FEG) was carried out at the Central Laboratories Sector of Egyptian mineral resources authority.

Preparation of ligand (BDBDA)

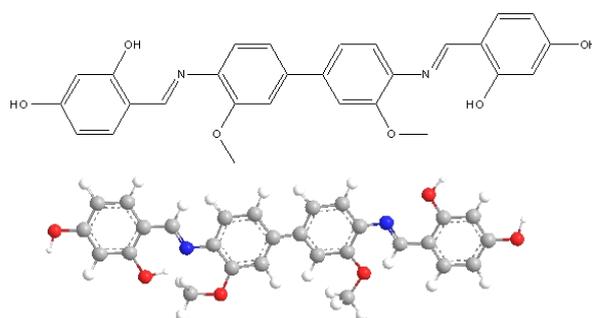
The ligand was prepared by using microwave method [5] in which the 3,3-Dimethoxybenzidine & 2,4- dihydroxybenzaldehyde were mixed in 1:2 molar ratio respectively and grinded very well in agate mortar and transferred to porcelain crucible and then the crucible put in microwave (with suction) for 3 -5 minutes and high yield (98%) of the N, N'-bis-(2,4-dihydroxybenzaldehyde)-3,3-Dimethoxybenzidine (BDBDA) ligand was obtained with the chemical formula C₂₈H₂₄N₂O₆ and chemical structure as shown in Scheme 1.

Preparation of solid complexes, and their evaluation as pigments

All the complexes were prepared by mixing equal molar ratio amounts of ligand BDBDA and the hydrated metal(II) acetate tetra[M = Cu^{II}, Ni^{II}]] in porcelain crucible without grinding, then the crucible put in the microwave for 5-7 min and the resulting complexes (Fig.1&2) were removed from microwave and cooled.

Evaluation of the prepared complexes as pigments

The prepared complexes were evaluated as pigments and the following tests were performed according the standard test methods of the American society of testing and materials (ASTM):(a) oil absorption (ASTM D:281-95, 1995) (b) hydrogen ion concentration (pH value) (ASTM D:1583-01, 2001), (c) bleed test (ASTM D:279-87, 1997), (d) fineness of dispersion (ASTM D:1210-96, 1996), (e) Moisture content (ASTM D:280-95, 1995).



Scheme 1. The chemical structure of ligand DBDBA.

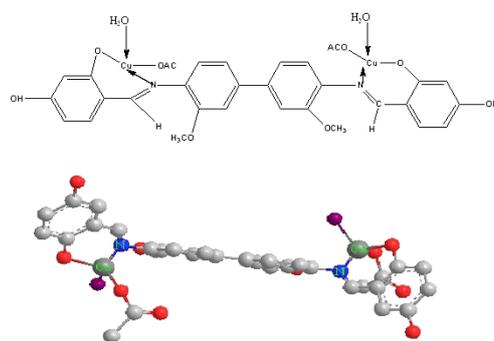


Fig. 1. The proposed Structure of Cu-BDBDA complex.

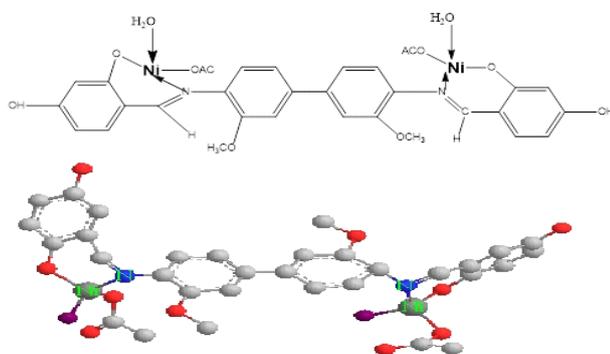


Fig. 2. The proposed Structure of Ni-BDBDA complex.

Paint preparation, evaluation and application

The paints were prepared by employing high stirring mixer and then they were introduced into a cold roll mild steel panels by using spray gun in a closed cabinet to give a dry paint film. The pigment is formulated in anticorrosion paint formula based on epoxy resin as anticorrosive binder according to conditions stated in Table 1.

TABLE 1. Anticorrosion paint formula.

Ingredients	Conc. (%)
⁽¹⁾ Epoxy resin	25.5
Silanol functional silicone resin (dispersing agent)	0.2
N-Butanol	6
Aluminum silicate	20
Mg ₃ Si ₄ O ₁₀ (OH) ₂ (talc powder)	13
BaSO ₄	12
Prepared complex	5
Xylene	2
Fumed silica	2
Organic clay	0.7
Polymethyl siloxane (antifoaming agent)	0.1
Polyether copolymers (leveling agent)	0.2
Methyl ethyl ketone	13.3
Curing agent (polyamide)	12.5

(1) Epoxide Equivalent Weight (g/eq): 430, Density @ 25°C (g/ml): 1.09, Non-volatile Content (wt%): 74-76.

Various methods have been applied for testing and evaluation of the prepared paints as follows:

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Physical and mechanical tests

A variety of physical and mechanical evaluations of the paint films were carried out on prepared steel panels [ASTM D 609-00] such as (a) determination of the dry paint film thickness [ASTM D 4138-07, 2007]; (b) measuring of adhesion using adhesive tape [ASTM D 3359-97, 2005]; (c) resistance of organic coatings to the effects of rapid deformation (impact) [ASTM D 2794-93 (Reapproved 1999)].

Corrosion tests

The coated steel panels were put in a salt spray cabinet at a temperature of 35°C, a moisture of 100% and a test solution of 5% NaCl concentration for 500h [ASTM D: B117-03]. The films were then examined for any defects such as rusting [ASTM D 6294-98, 2007], blistering [ASTM D 714-07, 2007], and scribe failure [ASTM D1654 -08]. Photographic inspection and grading of the paint films according to standard methods were carried out at the end of the test for a completion of corrosion resistance measurements (Fig. 8). A cross lines in the middle of each panel was made using a cutter to permit the salt solution to penetrate the panel to examine adherence of paint over the painted area.

Determination of chromatic characteristics

The chromatic characteristics of a substance are defined by the colorimetric or chromaticity coordinates: clarity (L^*), red/green colour component (a^*), and blue/yellow colour component (b^*); and by its derived magnitudes: chroma (C^*), tone (H^*) and chromacity [(a^*, b^*) or (C^*, H^*)], Overall colorimetric difference between two samples ΔE^* is defined according to the following mathematical functions:

The colour measurements were obtained by using the X-Rite RM200QC instrument, which is Imaging Spectro-colorimeter bridges for the gap between colour appearance and material colour. The device is automatically measuring the above mentioned parameters (ΔE^* , ΔL^* , Δa^* , Δb^* , ΔC^*)[6].

Results and Discussion

All the analytical, physical and spectroscopic data of the Schiff bases and their isolated metal complexes are given in Tables 2 and 3. The complexes are air stable for a long time and are soluble in DMF & DMSO.

Infra-red spectra

Infrared spectra of ligand

The positions of the significant IR bands of N, N' bis (2,4-dihydroxybenzaldehyde)-3,3 Dimethoxyanizidine (BDBDA) and their metal complexes are summarized in Table 3. The IR spectra of BDBDA show a strong band at 1621 cm^{-1} assignable to $\nu(\text{C}=\text{N})$ of the azomethine. The observation of this band confirms the formation of the azomethine linkage. The ligand also has

a strong band in the region 787–844 cm^{-1} corresponding to the out-of-plane deformation of the aromatic rings. The observation of broad weak bands in the 2600–3500 cm^{-1} region BDBDA ligand is taken as an evidence for the existence of intermolecular hydrogen bonding of the type OH...N [7,8].

Cu^{II} and Ni^{II} complexes

The IR spectral data (Table 3) of these complexes indicates that the ligand BDBDA behaves in a tetradentate manner with two Cu^{II} ions and two Ni^{II} ions, respectively through azomethine and deprotonating OH groups. This behavior is supported on the basis of the following evidences (i) the bands due to $\nu(\text{OH})$ and $\delta(\text{OH})$ of the ligand BDBDA have decreased in their intensity with a red shift, indicating the deprotonating of OH groups for BDBDA (ii) the shift observed in the $\nu(\text{C}-\text{O})$ frequency (iii) the negative shift of the azomethine group to lower wavenumber suggesting the involvement of this group in bonding (iv) the splitting of $\nu(\text{C}=\text{N})$ of BDBDA complexes suggests the presence of two types of azomethine groups. The two bands observed at 1543, 1437 cm^{-1} and 1580, 1436 cm^{-1} attributed to ν_{as} and ν_{s} carboxylic modes of Cu and Ni complexes respectively, elucidate the presence of acetate ion in the proposed structures in Fig. 1[9-11].

¹H NMR spectra of ligand

The ¹H NMR spectra of the ligand were recorded in DMSO (Figure 3). The proton NMR spectrum data of the ligand as shown in Table 2 indicates the appearance of a singlet signal in the range of 3.94 – 3.99 ppm due to the presence methyl protons. In the aromatic region; a few doublets and some overlapping doublets/multiplet are observed at range 6.2-7.5 ppm. These signals are due to the protons of benzene rings. The signals due to azomethine protons (-CH=N-) appeared as a singlet at 8.85 ppm. Another singlet corresponding to one proton is observed in the range 14.3 ppm is due to phenolic-OH group [12].

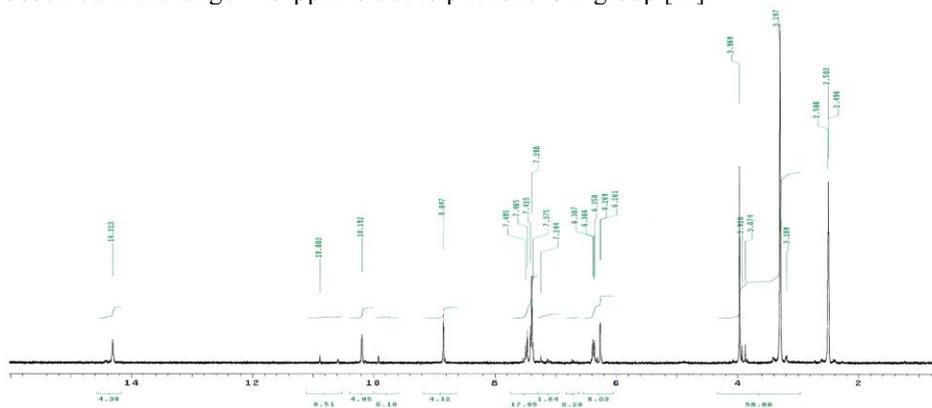


Fig. 3. The ¹H NMR spectroscopy of Ligand (BDBDA).

UV-Visible reflectance and Magnetic properties

The electronic spectra data of BDBDA in Table 3 showed the bands that observed at 375 and 412 nm which are assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligand respectively. The electronic spectra data of Cu (II) complex in Table 3 (Fig. 7) exhibit two bands at 676 nm and 339 nm (Cu-BDBDA Transitions) due to the $2B1g \rightarrow 2Eg$, $L \rightarrow M$ (C.T) transitions, and magnetic data shows μ eff value 2.19 B.M corresponding to the presence of one unpaired of electron which is consistent with tetrahedral geometry.

The μ eff value 2.94 B.M obtained for the Ni(II) complex is in good agreement with the tetrahedral geometry and the electronic spectra of Nickel complex in Table 3, appears two bands may be assigned to d-d transition which exhibit in the range of (460 nm) and (373 nm). These bands may be assigned to the two spin-allowed transitions $1A1g (D) \rightarrow 1A2g (G) (\nu_1)$, and $1A1g (D) \rightarrow 1B2g (G) (\nu_2)$ respectively [13-16].

TABLE 2. Analytical, physical and spectroscopic data of the Schiff base ligand and its related metal complexes.

Compound	M.p(°C), colour	Theoretical (found) % C N H	¹ H NMR Chemical Shift (δ p.p.m.)	ESR Parameters
Ligand (BDBDA)	315, Orange	69 5 5.8 (68) (5.18) (5.7)	14.3 (OH), 8.85 (CH=N,s,2H), 3.9(OCH ₃), 6.2-7.5 (ring,m,18H)	g_{\parallel} (2.11), g_{\perp} (2.19)
[Cu ₂ (BDBDA-2H) (OAC) ₂ (H ₂ O) ₂]	>370, Yellowish Brown	50.3 3.7 4.2 (50.5) (3.7) (4.9)		
[Ni ₂ (BDBDA- 2H)(OAC) ₃ (H ₂ O) ₂]	>370, Yellow	50 3.5 4. (48) (3.6) (5)		

TABLE 3. Significant IR, UV-Reflectance and magnetic data of Schiff base ligand and its metal complexes.

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\delta(\text{OH})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{OAC})_{\text{vas}}$	$\nu(\text{OAC})_{\text{vs}}$	$\lambda_{\text{max, nm}}$ (B.M) (assignments)	μ_{eff}
Ligand (BDBDA)	3500	1621	1320	1020	-	-	-	-	375($\pi \rightarrow \pi^*$), 412($n \rightarrow \pi^*$)	
[Cu ₂ (BDBDA-2H)(OAC) ₂ (H ₂ O) ₂]	3478	1616	1338	1261	490	309	1437	1543	676 L \rightarrow M(C.T), 339 (${}^2\text{B}_2 \rightarrow {}^2\text{E}_g$)	2.19
[Ni ₂ (BDBDA-2H)(OAC) ₂ (H ₂ O) ₂]	3308	1595	1227	1191	617,501	312	1436	1580	460(${}^1\text{A}_{1g}(\text{D}) \rightarrow {}^1\text{A}_{2g}(\text{G})$) 373(${}^1\text{A}_{1g}(\text{D}) \rightarrow {}^1\text{B}_{2g}(\text{G})$) (ν_2)	2.94

Thermal studies

Thermal Analysis of all complexes was carried out by the TGA, DTA techniques. The experimental results revealed that the degradation occurred in multiple stages, following a complex mechanism. For each stage, the kinetic parameters and thermogravimetric characterization have been estimated. The thermal behavior of all complexes explains as followed: the TG curves follows the decrease in sample mass with an increase in temperature. In the present investigation, heating rates were suitably controlled at 10 °C/minute and mass loss followed up to 25 – 1000 °C. The copper complex slowly studied the decomposition between 240 and 480 °C (Fig. 4). The first mass loss occurring at temperature >240 °C attributed to the removal of coordinated H₂O and the acetate molecules, the mass loss occurring at temp 240 – 340 °C correspond to the decomposition of part of organic ligand, then mass loss at temp 340-480 is attributed to the decomposition of the residue part of ligand molecules. The final product of the thermal decomposition at 480– 1000 °C might be referring to the presence of metal oxide [17].

On the other hand, the nickel complex studied the decomposition between 150 and 382 °C (Fig. 5). The first mass loss occurring at temperature 300 °C attributed to the removal of crystalline and coordinated H₂O and the acetate molecules in the complex meanwhile the mass loss occurring at temp 300 – 382 °C correspond to the decomposition of organic ligand molecules. The final product of the thermal decomposition at 382 – 1000 °C might be referring to the presence of metal oxide [18].

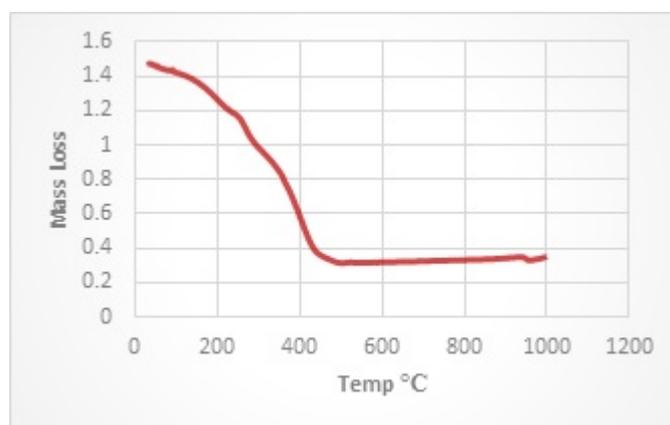


Fig. 4. Thermal gravimetric analysis Cu-BDBDA.

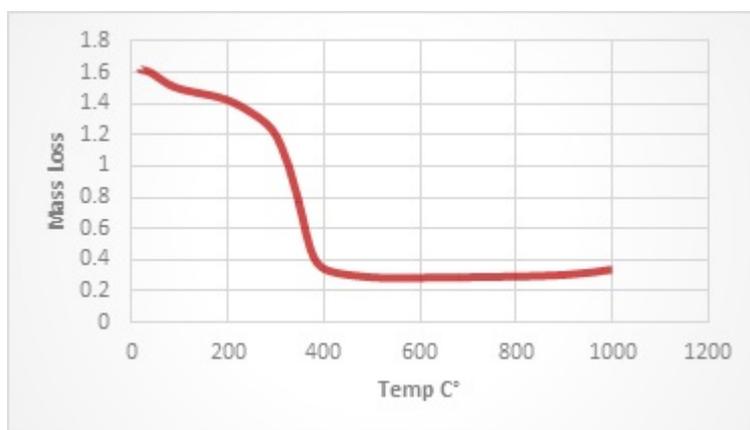


Fig. 5. Thermal gravimetric analysis Ni-BDBDA

Electron Spin Resonance (ESR)

ESR spectra of powdered sample of [Cu-BDBDA] exhibits an axial signal with two g values at 298 K, (Table 2, Fig. 6). The axial signals were analysed by the procedure given by Hathaway and Billing. The g_{\parallel} and g_{\perp} values (table 2) are >2.04 , consistent with copper (II) in axial symmetry with all the principle

axes aligned parallel. These g values indicate a tetrahedral stereochemistry. On the other hand, the calculated G value for the Cu^{II}-L is lesser than 4, indicates the exchange interaction between the copper centres [19,20].

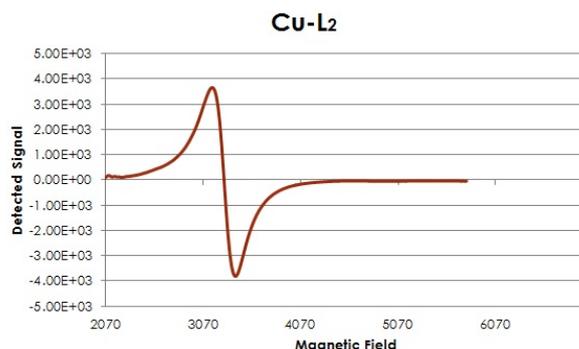


Fig. 6. ESR spectra at copper (II) complex at 298 k in the solid state.

Scanning Electron Microscopy

The morphology of the copper complex is performed with SEM and Fig. 7 shows that Cu-BDBDA which appear as bacillus shape with diameter width (80-90 nm) and bacillus particles are aggregated together to form amorphous shape with no porous structure which explain the lower values of oil absorption. These bacillus particles provide a reinforcing effect reducing the water and gas permeability and therefore imparted good anticorrosive properties and special appearance to the paint film when used in paint formulations.

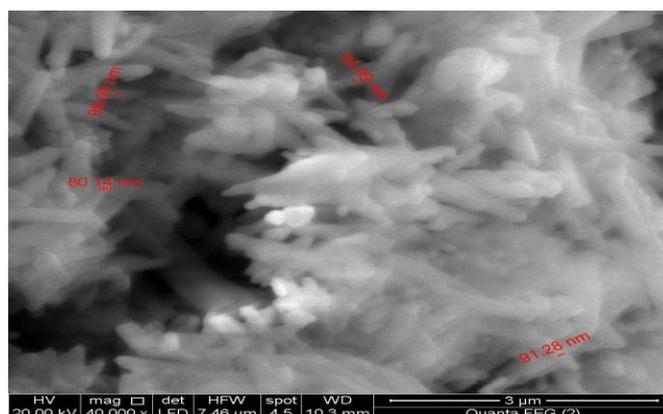


Fig .7. SEM photo of the copper complex Cu-BDBDA.

*Evaluation of the prepared complexes as pigments for paint application.**Physical properties of the prepared complexes*

The prepared complexes are evaluated as pigments before using in the corrosion resistance paints formulations and the following test methods (Table 4) cover the procedures for determining certain properties of pigments according to ASTM Standards.

Based on the results summarized in Table 4, it was noticed that all the synthesized complexes are alkaline in nature according to pH values. It is clear that the oil absorption values of Cu-BDBDA complex were the highest among the group, whereas Ni-BDBDA complex was the lowest. As the oil absorption value increased, more binder is needed to completely wet the pigment and form a homogeneous paint film and vice versa.

The moisture contents in all samples are neglectable which is referring to the stability of the complexes for the storage for long time and don't effect on their compatibility with the paint media. The fineness (degree of dispersion) test covers the measurement of the degree of dispersion (commonly referred to as "fineness of grind") of the pigment in a pigment-vehicle system such as liquid coatings and their intermediates., The fineness results of the samples indicated that all prepared complexes are highly dispersed in pigment-vehicle. The bleeding test determines the amount of colour produced when the pigment is in direct contact with different solvents. The bleeding tests implying a high degree of stability of the prepared pigments. Moreover, the bleeding results indicated that there is no bleeding (none perceptible colour)[21].

TABLE 4. The results of performance tests for the prepared complexes as pigments.

Complexes	pH	Oil absorption	Moisture Content	Fineness	Bleeding							
					T	EG	BAc	N.B	MEK	CH ₂ Cl ₂	CHCl ₃	CCl ₄
Cu- BDBDA	7.9	57%	0.33	7H	N	N	N	N	N	N	N	N
Ni- BDBDA	7.9	51.5 %	0.7	7H	N	N	N	N	N	N	N	N

[H= Hegman (fineness unite), T=Toluene, EG=Ethylene Glycol, BAc =Butyl Acetate, N.B=Normal Butanol, MEK=Methyl Ethyl Ketone, N=None.]

Physical and mechanical properties of the painted films

Based on the results of the physical and mechanical properties of dry paint films with & without prepared complexes given in table 5, the prepared films exhibit high film performance when the coating of 120 μm thickness was applied to the surface. Physical and mechanical properties of the coating composition were not affected by the different prepared complexes.

TABLE 5. Results of Impact, Dry film thickness and Adhesion for painted films based on the prepared complexes.

Compounds	Impact	Dry Film Thickness	Adhesion
Blank Sample	Pass	120 μm	5A
Cu- BDBDA	Pass	120 μm	5A
Ni- BDBDA	Pass	120 μm	5A

[5A=No peeling or removal]

Corrosion resistance of the painted films

Anticorrosive protection by paints has recently been described as being a combination of a physical barrier, a chemical inhibitor, and an electrical resistor. Pigments are incorporated in paints in order to enhance the barrier effect and give the desired color with no effect on the properties of paint's film. In the current work the corrosion properties of the paints based on the prepared complexes were studied to investigate if there is any effect of the prepared complex on the paint's film.

The results of corrosion resistance of the blank film and the painted films based on the prepared Complexes are given in Table 6 and Fig. 8 shows the photo of the painted films after salt spray test .The film thickness of the films ranges from 100 μm to 120 μm .

The blistering size is graded from 10 to 0, where 10 represents of no blistering and 0 representatives of the largest blister. Blistering frequency is denoted by F, M, MD and D (few, medium, medium dense and dense). Painted, or coated, specimens subjected to a corrosive environment are also evaluated by recording the average (mean) maximum and minimum creep age from the scribe mark. Scribe failure is also rated on a scale from 10 to 0, with 10 being zero (mm) from the scribe mark and 0 is 16 (mm) from the scribe mark. Rust grade 10 represents no rusting or less than 0.01% of surface rusted; rust grade 0 represents approximately 100% of surface rusted.

TABLE 6. Results of corrosion resistance of painted films based on the prepared complexes.

Painted film	Blistering		Scrub failure(mm)		Rust grad
	Size	Frequency	Area Failed %	Rating Number	
Blank Sample	9	F	1	9	9
Cu- BDBDA	7	MD	2	7	9
Ni- BDBDA	8	F	1	9	9

Chromatic characteristics of painted films

The results of colour characteristics of the painted films based on the prepared complexes before and after salt spray test are listed in Table 7. The results shows that the ΔE values for the painted films after salt spray test were

less than one, which indicates no change in the colour of the films before and after exposure to the corrosion conditions which is referring to the colour stability of the painted films, hence explains the stability of the prepared complexes when they used as anticorrosive metal complex pigments.

TABLE 7. Results of chromaticity coordinates of painted films before and after salt spray test.

Complex	Before salt spray test					After salt spray test				
	L*	a*	b*	C*	h	L*	a*	b*	h	ΔE
Cu- BDBDA	78.9	8.8	35.4	36.5	76	78.5	8.9	35.2	75.8	0.7
Ni- BDBDA	71.2	16.9	81.1	82.9	79.9	71.2	16.7	80.8	79.9	0.8

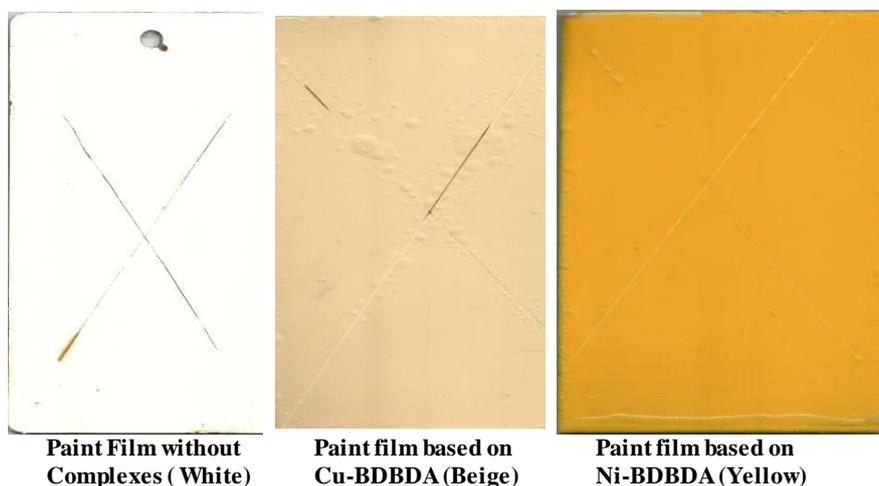


Fig. 8. Photograph of the painted films with and without the prepared complexes after salt spray test.

Conclusion

- The organic ligands and their metal complexes were successfully prepared by microwave method (Green Chemistry) and high yield is obtained.
- The physical properties of the prepared complexes (Fineness, Moisture content, bleeding), signified good performance materials.
- The prepared metal complexes can be used as pigments in the field of anticorrosion paints with no side effects on the paint formula.
- The Paint films based on the prepared complexes exhibited good mechanical properties (impact, adhesion).
- The Paint films based on the prepared complexes exhibited good corrosion resistance properties.

- There was no difference in the color properties of the painted films before and after corrosion conditions which is referring to the stability of the color of the prepared complexes.

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تحضير و دراسات طيفيه لبعض متراكبات قواعد شيف المعقد لعناصر النحاس والنيكل وتطبيقاتها كمخضبات ملونه فى صناعة دهانات الحمايه

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يهدف هذا البحث الى تحضير وتوصيف مركبات معقدته تحتوى على عناصر النحاس والنيكل بطريق سهله باستخدام جهاز الميكرويف وذلك عن طريق تفاعل متراكبات قواعد الشيف) المترابط (مع املاح النيكل والنحاس لتكوين متراكبات معقدته يمكن تطبيقها كمخضبات ملونه فى صناعة دهانات الحمايه.

كما يتم ايضا تحضير متراكبات قواعد الشيف عن طريق تفاعل الالديهيد الاروماتى (2,4 ثنائى الهيدروكسيل بينزالدهايد (مع الامين الاروماتى 3, 3) ثنائى الميثوكسى بينزيدىن (ليبتكون مترابط شيف الذى يتم تفاعله مع املاح النحاس والنيكل.

• ثم يتم قياس الخواص الفيزيائيه والتركييب الجزيئى لجميع المركبات التى تم تحضيرها باستخدام بعض التحاليل مثل تعيين نسبة الكربون والهيدروجين والنيتروجين، الأشعه فوق البنفسجيه ، الرنين النووى المغناطيسى، الأشعه تحت الحمراء وجهاز القابليه المغناطيسه وجهاز القياسات الحراريه وجهاز المسح للإلكترونى.

• كما تم تقييم المركبات التى تم تحضيرها كمخضبات فى صناعة دهانات الحمايه طبقا للمواصفات القياسيه الامريكيه (ASTM) وأظهرت النتائج ان المركبات التى تم تحضيرها يمكن استخدامها كمخضبات لدهانات الحمايه دون ان يكون لها تأثير على مكونات الدهان الاخرى.